Supporting Information

Upconversion Luminescence Enhancement in Plasmonic Architecture

with Random Assembly of Metal Nanodomes

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Fig. S1 Structure of UCNCs on the flat BR (a-e) and the glass ref (f-j). (a) and (f) are for the schematic diagrams of the UCNCs monolayer on the ZnO or glass substrate. (b) and (g) are for the SEM images of the UCNCs monolayer accompanied by the Voronoi tessleation constructed around the center coordinates of the individual UCNCs (numerically processed from SEM images). In the Voronoi tessellation, 4-, 5-, 7, and 8-neighbored cells are depicted with yellow, red, green, and blue colors. (d) and (i) are for the 2D maps of the structure factor in the 2D reciprocal space (q_x and q_y), which correspond to the numerically constructed diffractogram of the UCNCs monolayer. In the maps, the first and second hexagonal rings imply the UCNCs monolayer form nearly close-packed triangular lattice-type array on the substrate. (e) and (j) are for the 2D histogram maps showing the combined distribution of inter-distance (d_c) and diameter (D) of the UCNCs. At the lower and left edges, independent histogram for and are provided. From (e) and (j), it can be confirmed that the UCNCs monolayer is nearly close-packed array with nearly uniform size and inter-distance.



Fig. S2 (a) The PL results for the pNDA BR samples with respect to the deposition thickness (5, 10, 15 nm) of Ag film on ZnO layer (b) The integrated PL results at green and red emissions for the pNDA BR with respect to the deposition thickness (5, 10, 15 nm) of Ag film on ZnO layer.



Fig. S3 A schematic illustration of the 972 nm cw laser irradiation system for the UCL measurement. It is noted that all the PL measurements are performed by using an integrating sphere.



Fig. S4 A schematic energy level diagram for the upconversion luminescence mechanism via energy transfer from Yb³⁺ to Er³⁺ states. Black and blue dashed arrows indicate electronic transition and energy transfer, respectively. Dotted arrows mean multi-phonon relaxation and solid arrows represent emission process. Most IR light is absorbed by Yb³⁺ ions. Then some of the excited energy is transferred from Yb³⁺ to Er³⁺ and ground electrons of Er³⁺ ions are excited to ⁴I_{11/2} state. These electrons are excited to the higher ⁴F_{7/2} state via successive energy transfer from Yb³⁺ to Er³⁺. After relaxations, green and red emission peaks are generated via electronic transitions from ²H_{11/2}, ⁴S_{3/2}, and ⁴F_{9/2} states to ⁴I_{15/2} state, respectively.¹



Fig. S5 The UCL intensity measured at red and green emission as a function of thickness of the dielectric layer (ZnO) for the pNDA BR.



Fig. S6 (a) A simple approximation model to calculate the effective radiative and non-radiative decay rates of the UCNCs. Symbols denote the radius of the Ag NDA (R_s), the radius of the UCNC (R_u), interdistance (d), and $\delta \equiv d/2R_u - R_s/R_u$. (b) Schematic illustration of a cross section of the pNDA BR. The first shell means that the nearest UCNCs from the Ag NDA; the second shell is very next to the UCNCs in the first shell; the third shell is located right close by the UCNCs in the second one.



Fig. S7 A 2D map for the relationship of $\phi^{[1]}$ (a) and $\phi^{[3]}$ (b) as a function of the structural parameters κ and δ .

Properties	Electric permit	ttivity at 972 nm	Refractive index at 972 nm		
	$\varepsilon = \varepsilon_1 + i\varepsilon_2$		$\widetilde{n} = n + i\kappa$		
Material	ε ₁	ε2	n	к	
Ag BR, Ag nanodomes ²	-43.331	2.605	0.197	6.585	
ZnO ³	3.782	0	1.944	0	
UCNCs ⁴	2.560	1.487×10^{-4}	1.600	4.679×10 ⁻⁵	

Table S1. List of optical properties of silver, ZnO, and UCNCs monolayer implemented in optical simulation



Fig. S8 The reproducibility test for steady-state PL measurements of the pNDA BR. The five pNDA BR samples were measured five times (25 measurements in total). We observed that the experimental variations for the measured PL intensity were 7.54 % (*i.e.*, average intensity of 7.89×10^4 with standard deviation of 5.95×10^3) and 7.52 % (*i.e.*, average intensity of 2.30×10^5 with standard deviation of 1.73×10^4) for green and red emissions, respectively. We confirmed that the experimental observations can be reproducible within an acceptable experimental error range.



Fig. S9 The reliability test for steady-state PL measurements of the pNDA BR. The beam spot size of employed laser was 2.13×10^{-2} mm² that is much larger than the dimension of the Ag nanodomes and their array (*i.e.*, average diameter of 140 nm and average center-to-center distance of 320 nm). It was calculated that 2.30×10^5 of Ag nanodomes can be affected by the laser beam, and this number indicates the photonic and optical properties are represented by sufficiently large number of Ag nanodomes. To obtain reliability in the PL measurement, we re-obtained PL data using the pNDA BR by randomly choosing excitation positions with spot size of 2.13×10^{-2} mm². The level of PL intensity variation was 4.88 % (*i.e.*, average intensity of 1.56×10^5 with standard deviation of 7.63×10^3) and 3.85 % (*i.e.*, average intensity of 5.00×10^5 with standard deviation of 1.92×10^4) at green (541 nm) and red (661 nm) emissions, respectively.

Discussion on the comparison between enhancement factors from FDTD simulation and that from PL measurement results

The FDTD analysis was done to analyze E-field distribution in the layer of UCNCs confined in the randomized array of the metal nanodomes. The calculated EF for pNDA BR and the flat BR with respect to the glass ref in the optical simulation were 30.85 and 3.95, respectively. These values are not intended to provide any predicted values, but were intended to calculate emission quantum yield for the pNDA BR and the flat BR compared to the glass ref. It is well known that the enhancement of the absorbed E-field in the specific layer is not readily measured in an experimental manner such as using absorbance spectra. Instead, robust optical simulations such as FDTD have been extensively employed to quantitatively 'measure' the amount of E-field inside a particular region. This is mainly due to the fact that it is considerably difficult to precisely extract the absorbance spectra. In contrast, it is possible to experimentally measure overall enhancement in the PL intensity using an integrating sphere. Therefore, as shown in eq. (1), we were able to calculate the relative quantum yield for the emission using the FDTD results and experimentally measured PL intensities.

Calculation of the decay times from the measured TRPL

We quantitatively calculated the decay rates for the three different cases measure at green and red emission, respectively. In a simple manner, measurement of half-life (τ) at the half the initial PL intensity (I_0) on the basis of the single exponential decay behavior has been frequently employed to deduce the decay rate ($\Gamma \sim 1/\tau$). However, we used the stretched exponential decay dependence in order to obtain more accurate physical entities. The upconversion luminescence process involves multiple decay pathways such as quenching, radiative, and non-radiative processes. For the evaluation of the decay rate, we assumed that the overall decay can be lumped into a single exponential function, which dominates the other possible exponential functions. This approximation was used to simplify the analysis of the lifetime of exciton corresponding to the upconversion luminescence. Indeed, a number of studies on the upconversion luminescence have employed the single exponential decay model to approximately calculate the lifetime of luminescence.^{5–11} The good fitting quality can also be observed in **Fig. 3** for both green and red emissions. By using the stretched dependence for the decay curve fitting, we are assuming that the Ag nanodomes array (NDA) combined with UCNCs monolayer over the substrate is not perfectly ordered and photo-excited carriers diffuse in a dispersive manner.^{12,13}

The decay behavior can be expressed as follows:

$$\frac{I}{I_0} = \exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right).$$
(S1)

where β is the dispersion coefficient.^{12,13} By fitting the TRPL data with Equation (S1), we could obtain decay times for the three different cases (*i.e.*, glass, flat BR, and pNDA BR) measured at red and green emission, respectively, as shown in **Fig. 3**. As apparent from the figure, the TRPL data fit well with the stretched exponential dependence with high statistical correlation coefficient. The decay rate increases as introducing Ag NDA to the UCNCs as expectedly (*i.e.*, $\tau = 351.3 \ \mu s \rightarrow \tau = 188.3 \ \mu s$ at green and $\tau = 323.5 \ \mu s \rightarrow \tau = 198.8 \ \mu s$ at red emission, respectively).

Calculation of radiative and non-radiative decay rates

To analyze plasmonic effect on the radiative decay rate in the UCNCs on the pNDA BR, the TRPL data were taken at the saturated excitation power level. Using the linear proportionality between the QY ratio and PL emission ratio such that $\frac{QY_{(P)}}{QY_{(G)}}\Big|_{preen} = \left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right) \left(\frac{\tau_{(G)}}{\tau_{(P)}}\right)$, where $\tau_{(I)}$

and $\tau_{r(I)}$ denotes the overall and the radiative decay time of the system (I), we can deduce the following relationship between the ratios of the radiative decay rate in the cases of the p NDA BR and glass ref:

Weak:
$$\left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right)\Big|_{green} = 20.28, \left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right)\Big|_{red} = 42.20,$$

Saturated: $\left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right)\Big|_{green} = 2.73, \left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right)\Big|_{red} = 2.81.$ (S2)

As reported by Saboktakin *et al.*,¹⁴ it can be observed that the non-radiative decay rate of the UCNCs is highly enhanced in proximity to the metal nanoparticles, especially for Ag NDA. This proximity-driven effect can also be theoretically predicted.¹⁵ That is, other UCNCs that are not right next to the Ag NDA do not suffer the enhancement of the non-radiative decay rate. This can be true when the size of the UCNCs is not too small compared to the Ag NDA and the inter-distance among Ag NDA. In this linear approximation, we assumed that the Ag NDAs are arranged in a hexagonal array as shown in **Fig. S6a**; the UCNCs size is 30 nm, while that of the Ag NDA is 140 nm with an edge-to-edge distance of 180 nm between the NDA. This comparison of sizes allows us to construct the following simple linear approximation model to calculate the effective non-radiative decay rate of the UCNCs, Γ_{nr} , in the pNDA BR

$$\Gamma_{nr} = \Gamma_{nr}^{[0]} \left(1 - \phi^{[1]} \right) + \Gamma_{nr}^{[1]} \phi^{[1]}, \qquad (S3)$$

where the superscript [0] denotes the intrinsic value of Γ_{nr} , and [1] represents the enhanced rate for the UCNCs in the first shell. We employed the number fraction of the UCNCs in the first shell as shown in **Fig. S6b**, $\phi^{(1)}$, as the weight factor, and $\phi^{(1)}$ can be easily calculated as follows:

$$d = 2R_s + 2R_u \cdot \delta$$

$$N_{(1)}^{UC} = \left\{ \pi \left(R_s + 2\delta \cdot R_u \right)^2 - \pi R_s^2 \right\} \times \frac{1}{2} \quad \text{in this case, } \delta = 1$$

$$= \left(4\pi R_s \cdot R_u + 4\pi R_u^2 \right) \times \frac{1}{2}$$

$$= 2\pi R_u \left(R_s + R_u \right) \quad \text{first shell area for UCNCs.}$$

$$\phi^{[1]} \approx \frac{2\pi R_u \left(R_s + R_u\right)}{\frac{\sqrt{3}d^2}{4} - \frac{\pi R_s^2}{2}} = \frac{2\pi R_u \left(R_s + R_u\right)}{\frac{\sqrt{3}}{4} \left(2R_s + 2R_u \cdot \delta\right)^2 - \frac{\pi R_s^2}{2}} = \frac{4\pi \left(1 + \kappa\right)}{2\sqrt{3} \left(\delta + \kappa\right)^2 - \pi \kappa^2}, \ \kappa = \frac{R_s}{R_U}, \ \delta = \frac{d}{2R_U} - \kappa,$$
(S4)

In the Equation (S4), we used a number-weighted linear approximation and assumed that the UCNCs have a sufficiently narrow size-distribution and maintain a closely-packed structure around the Ag NDA.

For the radiative decay rate, it should be noted that the spatial range of the plasmonic resonance effect is greater than the first shell range. Indeed, we calculated squared intensity of the EM field around the UCNCs array in a radial direction $(|E(r)|^2)$. We observed a few distinguishable peaks located at the edges of each of the UCNCs, and 96.7% of the integrated

squared EM intensity ($\int_{v_{U(m)}} |E(r)|^2$) is observed within the boundary of the third shell. Using

these calculation results, we can construct a simple linear approximation model to calculate the effective radiative decay rate of the UCNCs, Γ_r , in the pNDA BR as follows:

$$\Gamma_r = \Gamma_r^{[0]} \left(1 - \phi^{[3]} \right) + \Gamma_r^{[1]} \phi^{[3]}, \tag{S5}$$

In this linear approximation, we employed the number fraction of the UCNCs in the first, second, and third shells, $\phi^{[3]}$, as the weight factor, and $\phi^{[3]}$ can be easily calculated as follows:

If
$$\delta < \delta^*$$

$$\phi^{[3]} = 1, \ \delta^* = 3\sqrt{3} + \kappa \left(\frac{\sqrt{3}}{2} - 1\right)$$
else if $\delta^* \le \delta < 6$

$$A_0 = \frac{\sqrt{3}d^2}{4} - \frac{\pi}{2}R_s^2$$
divide by area for close-packed UCNCs, $2\sqrt{3}R_u^2$

$$\frac{A_0}{2\sqrt{3}R_u^2} = \frac{\sqrt{3}\left(\delta + \kappa\right)^2 - \frac{\pi}{2}\kappa^2}{2\sqrt{3}}$$

$$\phi^{[3]} = \frac{\frac{\pi}{2}\left[\left(\kappa + 6\right)^2 - \kappa^2\right]}{\sqrt{3}\left(\delta + \kappa\right)^2 - \frac{\pi\kappa^2}{2}}$$
third shell area for UCNCs divided by A_0

$$= \frac{12\pi(3 + \kappa)}{2\sqrt{3}(\delta + \kappa)^2 - \pi\kappa^2}.$$
(S6)

In **Fig. S6**, the relationships of $\phi^{[1]}$ and $\phi^{[3]}$ as functions of κ and δ are presented. In the colored maps, we observe that $\phi^{[1]}$ and $\phi^{[1]}$ commonly increase when both κ and δ are decreased. Then, using Equation (S3) and (S5), we extend our discussion to calculate the ratio of the decay rate between the pNDA BR and the glass systems as follows:¹⁶

$$\frac{\Gamma_{(P)}}{\Gamma_{(G)}} = \frac{\Gamma_{nr(P)} + \Gamma_{r(P)}}{\Gamma_{nr(G)} + \Gamma_{r(G)}} = \frac{\Gamma_{nr}^{[0]} \left(1 - \phi^{[1]}\right) + \Gamma_{nr}^{[1]} \phi^{[1]} + \Gamma_{r}^{[0]} \left(1 - \phi^{[3]}\right) + \Gamma_{r}^{[1]} \phi^{[3]}}{\Gamma_{nr}^{[0]} + \Gamma_{r}^{[0]}}, \qquad (S7)$$

where we assumed that $\Gamma_{nr(G)} \approx \Gamma_{nr(P)}^{[0]} = \Gamma_{nr}^{[0]}$ and $\Gamma_{r(G)} \approx \Gamma_{r(P)}^{[0]} = \Gamma_{r}^{[0]}$ considering that there was no metal-induced quenching or distinguishable plasmonic resonance in the glass case. Using Equation (S2)-(S7), we calculate the enhancement factors for the non-radiative decay rates of the PL such that

$$\Gamma_{nr}^{[1]}\Big|_{green} = 4.80 \Gamma_{nr}^{[0]}\Big|_{green}, \ \Gamma_{nr}^{[1]}\Big|_{red} = 3.75 \Gamma_{nr}^{[0]}\Big|_{red}.$$
 (S8)

From this calculation, we observe an increase in the total non-radiative decay rate, such that

$$\Gamma_{nr(P)}\Big|_{green} = 1.87 \Gamma_{nr}^{[0]}\Big|_{green}, \ \Gamma_{nr(P)}\Big|_{red} = 1.63 \Gamma_{nr}^{[0]}\Big|_{red}.$$
(S9)

Thus, the increase in the decay rate of the PL for the case of the pNDA BR is mainly governed by increases in the non-radiative decay rate irrespective of the excitation power. Nevertheless, it should be noted that the radiative decay rate increase caused by introducing the Ag NDA derived plasmon resonance is relatively higher than the increase in the non-radiative decay rate by introducing Ag NDA induced quenching effect for both green and red emissions (*i.e.*,

$$\left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right)_{green} \times \left(\frac{\Gamma_{nr}^{[0]}}{\Gamma_{nr(P)}}\right)_{green} = 10.84, \ \left(\frac{\tau_{r(P)}}{\tau_{r(G)}}\right)_{red} \times \left(\frac{\Gamma_{nr}^{[0]}}{\Gamma_{nr(P)}}\right)_{red} = 25.89 \quad \text{for green and red emissions,}$$

respectively, at the weak excitation power and ×1.46 and ×1.72 for green and red emissions, respectively, at the saturated excitation power). For the calculation, we assumed that $\Gamma_r^{[0]} \approx 10^{-3}\Gamma_{nr}^{[0]}$, which is supported by our experimental data and others.¹⁷ From the experimental

observations and Fig. S7, we used $\phi^{[1]} = 0.228$ and $\phi^{[3]} = 0.880$, respectively.

The analysis provided above indicates that there exists a quenching effect given by the Ag NDA for the nearest UCNCs, which is emerged as increase in the non-radiative decay rate of the emission, while the Ag NDA also give rise to plasmon effects on the UCNCs near the Ag NDA, which is observed as increase in the radiative decay rate of the emission.

Analysis of decay rate as a function of the excitation power

To examine the effects of the excitation power on the transition rate in the pNDA BR that can be represented by the TRPL data, we applied four different excitation powers at 972 nm. As shown in **Fig. S10**, it is evident that the excitation power exhibit nearly constant effects on the transition kinetics of the PL. In order to check the independence of the transition kinetics on the excitation power, we analyzed total decay rate from the quantum yield of the emission such that

Quantum yield
$$(\phi) = \frac{\# \text{ photons emitted}}{\# \text{ photons absorbed}} \propto \frac{PL \text{ intensity}}{\text{incident power}}$$
 (S10)

$$=\frac{\Gamma_{rad}}{\Gamma_{tot}}\tag{S11}$$

when
$$\Gamma_{tot} = \frac{1}{\tau_{tot}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{non}} = \Gamma_{rad} + \Gamma_{non}$$
 (S12)

where Γ_{tot} , τ_{tot} , τ_{rad} , and τ_{non} are the total decay rate, total decay time, radiative decay time, and nonradiative decay time, respectively. From the equations (S10) and (S11), we can

calculate the radiative decay rate as shown in Table S2.



Fig. S10 (a) TRPL data for red emission with the different excitation powers of the incident laser (at 972 nm) for the pNDA BR. (b) the integrated UCL intensity as a function of the excitation laser power density for the pNDA BR architecture measured at red emission that was already shown in the **Fig. 5(a)** in the manuscript. The four different power densities (19.5, 127.8, 242.5, and 343.0 mW) were denoted by dotted lines with the different colors

	PL intensity	Total decay	Decay rate		
Incident PL intensity power (mW) (a.u.)		time	Total	Radiative	Nonradiative
	$\left. \tau_{(P)} \right _{red} (\mu s)$	$\left \Gamma_{(P)}\right _{red}(1/s)$	$\left \Gamma_{r(P)}\right _{red}(1/s)$	$\left \Gamma_{nr(P)}\right _{red}(1/s)$	
19.5	0.009	181.96	5.50×10 ³	5.89	5.49×10 ³
127.8	0.074	169.63	5.90×10 ³	7.77	5.89×10 ³
242.5	0.148	167.78	5.96×10 ³	8.29	5.95×10 ³
343.0	0.212	166.64	6.00×10 ³	8.45	5.99×10 ³

Table S2. A list of power dependent PL intensity, total decay rate and calculated results



Fig. S11 The laser power dependence of (a) the radiative decay rate with inset for the laser power dependence of the radiative decay time, (b) the total and nonradiative decay rates with inset for the laser power dependence of the total and nonradiative decay times for the pNDA BR sample.

Table S2 summarizes the PL experimental results such as absorbed incident power, PL intensity, total decay time, total decay rate, radiative decay rate, and nonradiative decay rate of pNDA BR. We adopted the correction coefficient considering the absorption of 0.4390 based on the total reflection result at 972 nm into the quantum yield calculation. The lifetime is shown in the inset of **Fig. S11**. The lifetime gradually decreases as the incident power increases, which is in agreement with the reported results with regard to upconversion process.^{18,19} Now, we can obtain the radiative decay rate from equation (S10) and (S11). From this result, we can have following result as:

Table S3. List of the enhancement ratio of the decay rates and times at 343.0 mW to that at19.5 mW from the results in Table S2

Increase in	Enhancement values					
incident power PL inte	PL intensity	total decay time	total decay rate	radiative decay rate	nonradiative decay rate	
17.60	23.04	0.92	1.09	1.43	1.09	

In **Table S3**, the PL intensity enhancement is 23.04 times increased from 9.2×10^{-3} at 19.5 mW to 2.1×10^{-1} at 343.0 mW; the radiative decay rate enhancement is 1.43 times increased from 5.89 to 8.45 whereas the nonradiative decay rate enhancement is 1.09 times increased from 5.49×10^{3} to 5.99×10^{3} . The radiative decay rate enhancement is slightly enlarged as 1.43 times compared to the large increase in the excitation power as 17.60 times and the PL intensity as 23.04 times. From these results, we can find that the excitation power mainly concerns the PL increase rather than radiative decay rate, and imposes negligible effects on the overall and non-radiative decay rate.

Calculation of the geometric features of the Ag NDA on the ZnO layer

In the case of fluidic film of thickness h, the lateral flow in the film parallel to the substrate (x -direction) can be described using the following continuity equation:

$$\frac{\partial h}{\partial t} = C\nabla^2 P_{film}, \ P_{film} = \frac{A}{6\pi h^3} - \gamma \nabla^2 h \tag{S13}$$

where P_{film} is the pressure across the film, A is the effective Hamaker constant for the van der Waals interaction of the fluidic film (subscript f) between air (subscript a) and the ZnO layer (subscript b) (*i.e.*, $A \approx (A_a^{0.5} - A_f^{0.5})(A_b^{0.5} - A_f^{0.5})$), γ is the surface energy of the film, and C is the constant which is dependent of the film properties.²⁰ The dynamic instability of the fluidic film is mainly due to by this spontaneous amplification of the spatial fluctuation of the film thickness, and the fluctuation can be written by linear perturbation with the wave equation form such that ²¹

$$h(x,t) = h_0 + \varepsilon \exp(t / \tau_d) \cos(kx)$$
(S14)

where h_0 is the initial thickness of the film, ε is the amplitude of the fluctuation which is assumed to be much smaller than h_0 at initial state, τ_d is the characteristic time for the growth of fluctuation, and k is the wavenumber for the characteristic length scale corresponding to the dynamics instability. In Equation (S14), the spatial dimension was specified in x-direction without losing generality. With Equation (S13) and (S14), it can be found that

$$(C\tau)^{-1} = \frac{Ak^2}{2\pi h_0^4} - \gamma k^4$$
 (S15)

where the linear approximation of the perturbed state around the initial state in which $\partial h / \partial x \ll 1$ was used. The fastest growing perturbation governs overall fluctuation dynamics, and therefore, we can find the governing fluctuation mode by maximizing $(C\tau)^{-1}$ with respect to k such that

$$k_{C} = \frac{2\pi}{L_{C}} = \left(\frac{A}{4\pi\gamma h_{0}^{4}}\right)^{1/2}, \ \tau_{dC} = \frac{96\pi^{3}\lambda h_{0}^{5}}{A^{2}}$$
(S16)

where L_c denotes the characteristic length scale for the dynamics instability. In the case of the dewetting, L_c can be considered as average center-to-center distance of the dewetted droplets. In particular, we can find the height H and diameter W of the Ag NDA as a function of the contact angle of the Ag film on the ZnO surface (θ) and h_0 as follows:

$$H = R(1 - \cos\theta), W = 2R\sin\theta,$$

$$R = \left(\frac{3^{3/2}\Gamma^2 h_0^5}{4F(\theta)\pi}\right)^{1/3}, \Gamma = \left(-\frac{16\pi^3\gamma}{A}\right)^{1/2}, F(\theta) = \cos^2\theta - 3\cos\theta + 2,$$

$$L_c = 4\pi h_0^2 \left(-\frac{\pi\gamma}{A}\right)^{1/2}$$
(S17)

where γ is the surface energy of the Ag film. Equation (S17) is derived from: 1) the governing equation of the dynamic instability of a thin film in which an initial film thickness fluctuation is spontaneously growing (refer to Equation (S13)-(S16)) and 2) a relationship for the volume conservation of the distributed droplets, such that

$$\frac{\pi R^3 F(\theta)}{3} = \frac{L_c^2 3^{1/2} h_0}{4}$$
(S18)

where a triangular lattice assembly structure for the distribution of the Ag NDA is assumed. From Equation (S17), it is also found that the average height-to-diameter ratio of the Ag NDA at equilibrium (H/W) is a function of θ regardless of the initial film thickness, such that

$$\frac{H}{W} = \frac{\tan\left(\frac{\theta}{2}\right)}{2}.$$
(S19)

Using the observed average values of H and W, it is calculated that $\theta \sim 65^{\circ}$, which is consistent with the observed angle.

References

- 1 S. Heer, K. Kömpe, H.-U. Güdel and M. Haase, *Adv. mater.*, 2004, **16**, 2102–2105.
- 2 E. D. Palik, Ed., in *Handbook of Optical Constants of Solids*, Academic Press, Burlington, 2002.
- 3 W. L. Bond, J. Appl. Phys., 1965, 36, 1674–1677.
- 4 H. P. Paudel, D. Dachhepati, U. Gautam, K. Bayat and M. F. Baroughi, 37th IEEE Photovoltaic Specialists Conference, 2011, pp. 000920–000923.
- 5 Y. Lu, J. Lu, J. Zhao, J. Cusido, F. M. Raymo, J. Yuan, S. Yang, R. C. Leif, Y. Huo, J. A. Piper, J. Paul Robinson, E. M. Goldys and D. Jin, *Nat. Commun.*, 2014, **5**.
- 6 N. Liu, W. Qin, G. Qin, T. Jiang and D. Zhao, Chem. Commun., 2011, 47, 7671.
- 7 S. Zhao, S. Xu, G. Jia, D. Deng, L. Huang and H. Wang, *Mater. Lett.*, 2011, 65, 2407–2409.
- 8 Q. Cheng, J. Sui and W. Cai, *Nanoscale*, 2012, 4, 779–784.
- 9 W. Deng, L. Sudheendra, J. Zhao, J. Fu, D. Jin, I. M. Kennedy and E. M. Goldys, *Nanotechnol.*, 2011, **22**, 325604.
- 10Q.-C. Sun, H. Mundoor, J. C. Ribot, V. Singh, I. I. Smalyukh and P. Nagpal, *Nano Lett.*, 2014, **14**, 101–106.
- 11X. Wang, W. W. Yu, J. Zhang, J. Aldana, X. Peng and M. Xiao, Phys. Rev. B, 2003, 68.
- 12 H. Jayatilleka, D. Diamare, M. Wojdak, A. J. Kenyon, C. R. Mokry, P. J. Simpson, A. P. Knights, I. Crowe and M. P. Halsall, *J. Appl. Phys.*, 2011, **110**, 033522.
- 13 M. Dovrat, Y. Goshen, J. Jedrzejewski, I. Balberg and A. Sa'ar, Phys. Rev. B, 2004, 69, 155311.
- 14M. Saboktakin, X. Ye, U. K. Chettiar, N. Engheta, C. B. Murray and C. R. Kagan, *ACS Nano*, 2013, **7**, 7186–7192.
- 15R. Carminati, J.-J. Greffet, C. Henkel and J. M. Vigoureux, *Opt. Commun.*, 2006, **261**, 368–375.
- 16D. M. Wu, A. García-Etxarri, A. Salleo and J. A. Dionne, *J. Phys. Chem. Lett.*, 2014, **5**, 4020–4031.
- 17J.-C. Boyer and F. C. J. M. van Veggel, *Nanoscale*, 2010, **2**, 1417–1419.

- 18R. J. R. Vieira, L. Gomes, J. R. Martinelli and N. U. Wetter, *Opt. Express*, 2012, **20**, 12487–12497.
- 19K.-S. Lim, P. Babu, S.-K. Lee, V.-T. Pham and D. S. Hamilton, *J. Lumin.*, 2003, **102-103**, 737–743.
- 20S. Herminghaus, Phys. Rev. Lett., 1999, 83, 2359-2361.
- 21G. Reiter, Phys. Rev. Lett., 1992, 68, 75-78.